

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



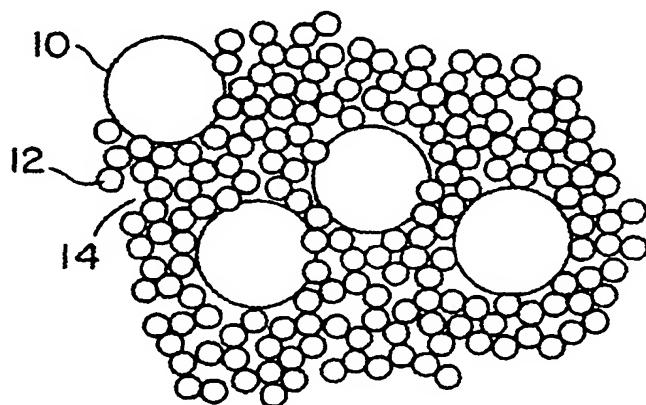
(43) International Publication Date
15 March 2001 (15.03.2001)

PCT

(10) International Publication Number
WO 01/17648 A1

- (51) International Patent Classification⁷: **B01D 15/00, A62D 3/00**
- (21) International Application Number: **PCT/US00/24472**
- (22) International Filing Date:
7 September 2000 (07.09.2000)
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
60/152,339 7 September 1999 (07.09.1999) **US**
- (71) Applicant (for all designated States except US): **INDUSTRIAL SCIENCE & TECHNOLOGY NETWORK, INC. [US/US];** Cyber Center, Suite 21, 1600 Pennsylvania Avenue, York, PA 17404 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **YANG, Arthur, Jing-Min [US/US];** 915 Dorsey Road, Lancaster, PA 17601 (US). **ZHANG, Yuehua [US/US];** 424 Waupelani Drive, Apt. D-21, State College, PA 16801 (US).
- (74) Agent: **STEINBERG, Richard, A.;** Sherman & Shalloway, 413 North Washington Street, Alexandria, VA 22314 (US).
- (81) Designated States (*national*): **AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.**
- (84) Designated States (*regional*): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**
- Published:**
— *With international search report.*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **NANOPORE REACTIVE ADSORBENTS FOR THE HIGH-EFFICIENCY REMOVAL OF WASTE SPECIES**



(57) Abstract: A nanoporous reactive adsorbent incorporates a relatively small number of relatively larger reactant, e.g., metal, enzyme, etc., particles (10) forming a discontinuous or continuous phase interspersed among and surrounded by a continuous phase of smaller adsorbent particles (12) and connected interstitial pores (14) therebetween. The reactive adsorbent can effectively remove inorganic or organic impurities in a liquid by causing the liquid to flow through the adsorbent. For example, silver ions may be adsorbed by the adsorbent particles (12) and reduced to metallic silver by reducing metal, such as irons, as the reactant particles (10). The column can be regenerated by backwashing with the liquid effluent containing, for example, acetic acid.

WO 01/17648 A1

NANOPORE REACTIVE ADSORBENTS FOR THE
HIGH-EFFICIENCY REMOVAL OF WASTE SPECIES

NON-PROVISIONAL APPLICATION
(35 USC 111(a))

This invention was made with Government support under Contract No. DE-FG02-97ER82409 awarded by the Department of Energy. The Government has certain rights to this invention.

Cross Reference to Related Applications

5 This application is related to Provisional Application No. 60/152,339, filed September 7, 1999.

Field of the Invention

This invention relates to nanoporous reactive adsorbents and to the use thereof in removing impurities from liquids.
10 More particularly, this invention relates to silica based nanoporous adsorbents having very high density of chemical surface modifying ligands further modified to include chemically reactive species and to the use thereof for purifying contaminated liquids.

15 Technology Background and Comparison with Existing Art

The most common method of removing waste species from a liquid stream is by adsorption. Such a method can be applied to water purification in a continuous operation with water flowing through a column or over a fixed bed of the solid
20 adsorbent. Commercial ion-exchange resins and carbon black filters are examples of this approach.

The common characteristics of an efficient adsorbent include a large surface area and connected (i.e. open) porous structure for fast diffusion. Recent developments in this
25 technical field include the incorporation of molecular recognition functional species (i.e. metal-binding ligands) onto the surface of various inorganic or organic carrier materials to achieve the selective adsorption of a particular group of ions out of the background ions. Among all the
30 carrier materials explored in this developmental field, the synthetic silica gel is the most widely studied. This is because the synthetic nanoparticle silica contains a large amount of active silanol groups on its surface, necessary for

the incorporation of metal-binding ligands, and has an exceptionally high surface area as well as open porous structure, necessary for achieving a rapid high-capacity adsorption.

5 Although much prior art has been developed based on the identical principle of incorporating metal-ion binding functional groups onto the surface of nanopore silica, the characteristics of the resulting silica-ligand composite products may differ significantly^{1,2,3,4,5,6,7} depending on the
10 routes of processing.

 Different processing techniques may start with silica gels similar in porosity and specific surface area (surface area per gram of silica) but could end up with products of distinctly different loading of the ligand groups. Or, two
15 composites may contain a similar amount of loading of functional groups and yet differ considerably in adsorption efficiency.

 One of the present inventors has recently developed an advancement in technology of the surface modification of low-
20 density silica gel (CSMG) which can produce high surface area silica with extremely high loading of functional groups that increases the adsorption efficiency and capacitance of the silica adsorbent to a significantly higher level; this technology is the subject matter of US application Serial No.
25 09/601,888, filed August 9, 2000, based on Provisional Application Serial No. 60/074,026, filed on February 9, 1998

¹ L. Mercier and T. Pinnavaia, Adv., Mater., 9, No. 6, pp 500-503 (1997)

² L. Mercier, C. Detellier, Environ. Sci. Technol., 29, p 1316 (1995)

³ M. S. Iamamoto, Y Gushikem, J. Colloid Interface Sci. 129, p 162 (1989)

⁴ E. I. S. Andreotti, Y Gushikem, J. Colloid Interface Sci. 142, p 97 (1991)

⁵ W. C. Moreira, Y Gushikem, O. R. Nascimento, J. Colloid Interface Sci. 150, p 115 (1992)

⁶ US Patent 5,814,226, September 1998, Lawrence L. Tavlarides, Nandu Deorkar

⁷ US Patent 5,817,239 October 1998, Lawrence L. Tavlarides, Nandu Deorkar.

and International PCT Application PCT/US99/02181, filed February 3, 1999, the disclosures of which are incorporated herein in their entirety by reference thereto.

The present inventors recognized that a high-capacity adsorption may lead to a much higher concentrated environment of adsorbed specie on the surface of an adsorbent when compared with the specie concentration in the passing stream. Such increased specie population density on the pore surface could significantly increase the reaction rate of the adsorbed specie with other reactants existing nearby. Moreover, the change in the electronic state of adsorbed specie during chemisorptions could also affect its reaction rate favorably. The adsorbent, therefore, could function as a heterogeneous catalyst for the chemical reaction of adsorbed species. If the adsorbed waste specie can be converted to a less harmful or even useful specie by such a reaction, the adsorbent then becomes a reactive adsorbent. The additional option of in-situ reaction to convert the adsorbed specie provided by a reactive adsorbent can significantly increase its treatment capacity because the converted waste species normally do not occupy the surface adsorption sites any longer. The present invention is based, in part, on the recognition and utilization of the foregoing considerations.

Summary of the Invention

This invention has been accomplished by embedding reactive species into the structure of a nanopore adsorbent in order to convert waste or undesirable species in situ during filtration as well as to increase the treatment capacity of the adsorbent towards a specific waste specie and/or recoverable specie having intrinsic value.

Thus, for example, the present invention, in one particular embodiment, provides for treating heavy metal ions in a waste stream. However, this invention may also be extended to other reactive adsorption applications by appropriate selection of the embedded reactive species.

In another aspect of the invention, there is provided a regeneration scheme that utilize the reactive nature of the nanopore adsorbent by applying backwash effluent repetitively through the reactive adsorbent to first remove the adsorbed species and then react them with the reactant embedded within the adsorbent. Such a regeneration scheme does not require additional treatment of the backwash effluent and is hereby given the name of close-end regeneration.

The above features of the present invention are accomplished according to one embodiment of the invention by a composite nanopore reactive adsorbent comprising

a continuous phase comprised of adsorbent particles and interstitial pores therebetween, and

a phase comprised of reactant particles contained in domains surrounded by the adsorbent particles and their interstitial pores, thereby forming an intimate admixture of adsorbent particles, reactant particles and interstitial pores,

wherein the size of the reactant particles is at least several times larger than the size of adsorbent particles such that the interstitial pores predominantly reside with the adsorbent particles, and

wherein the relative volume fraction of the interstitial pores in the continuous phase to that of the adsorbent particles is larger than the percolation threshold value so that the continuous phase contains connected open pores.

Preferably, in the above nanopore reactive adsorbent, the adsorbent particles are formed from precipitated silica or the adsorbent particles comprise chemically surface modified amorphous silica gel. In a preferred embodiment of this aspect of the invention, the reactant particles are comprised of metal effective as an in-situ reducing reagent, such as, for example, magnesium, aluminum, iron, and/or zinc. However, the reactant particles may be comprised of a solid redox reagent effective to react with an adsorbed species, or in

still another embodiment, the reactant particles are comprised of a catalyst, such as an enzyme, or other organic or inorganic catalyst, which is effective to react with an adsorbed species.

5 According to another aspect, the present invention provides a method for producing the composite nanopore reactive adsorbent as described above, comprising:

 reacting an inorganic metal oxide nanoporous gel precursor characterized by a plurality of open channels within
10 the gel structure and hydroxyl reactive groups on the surface thereof, with a coupling reagent reactive with said hydroxyl reactive groups, in an aqueous alcoholic medium under an inert atmosphere and at an elevated temperature within the range of from about 40°C to about 80°C to cause the coupling reactant
15 to condense and react with said hydroxyl reactive groups to form a grafted metal oxide sol;

 (b) mixing and stirring the grafted silica sol with reactant particles; and

 (c) gelling the stirred mixture from step (b).

20 In the above method, the gel precursor may comprise a silica gel precursor or the gel precursor may comprise an oxide of a metal selected from the group consisting of silicon, zirconium, aluminum, titanium, iron and lanthanum.

 In accordance with still another aspect of the invention,
25 there is provided a method for separating an inorganic or organic target specie from a liquid containing the target specie (e.g., a metal, such as silver; a microbiological contaminant, such as protein, viral particles; and the like) which comprises contacting the liquid with a nanopore reactive
30 adsorbent having a reactive embedded species among the interstitial pores thereof. For example, in the case where the target specie comprises silver ions, the reactant particles of the reactive adsorbent may comprise iron particles, whereby the adsorbed silver ions are reduced by the
35 iron particles to metallic silver. The recovered specie, e.g., silver metal, will preferably be recovered from the adsorbent.

In a particularly preferred embodiment of this aspect of the invention the nanopore reactive adsorbent is present in or as a filter medium.

According to still another aspect of the invention, there is provided a closed end regeneration method which comprises adsorbing a specie from a starting liquid containing the specie by contacting the liquid with a nanopore reactive adsorbent comprising connected interstitial pores having adsorption sites on the surfaces thereof, and containing among the interstitial pores thereof reactant particles which are reactive with said specie, to thereby remove at least some of said specie from said liquid, thereby forming spent adsorbent;

flowing a treating liquid through the spent nanopore reactive adsorbent to remove adsorbed specie from said adsorption sites and partially regenerate said reactant particles, thereby generating effluent treating liquid, and reflowing said effluent treating liquid through the treated spent nanopore reactive adsorbent at least once to regenerate said adsorption sites and said reactant particles.

Brief Description of the Drawings

Figure 1-A is a schematic view of nanopore reactive adsorbent according to the invention;

Figure 1-B is a schematic view of an alternative embodiment of nanopore reactive adsorbent according to the invention;

Figure 2 is a graph plotting silver adsorption as a function of Bed Volume for a conventional silica gel, a chemically surface modified silica gel (CSMG) and a iron-loaded silica gel adsorbent according to this invention; and

Figure 3 is a graph plotting amount (ppm) of adsorbed specie (Ag+) as a function of bed volume during adsorption with regeneration in accordance with one embodiment of the present invention.

Detailed Description of the InventionWorking Principles

A wet low-density silica gel normally contains a porous open-cell structure. Water flows and ions diffuse freely within this kind of open structure. Thus, the entire surface area of the pores can be accessed rapidly. The open porous structure will increase the efficiency and speed of ion adsorption in a water treatment operation. In addition, such an open structure is necessary for the incorporation of large functional groups onto the entire surface. Without an open structure, the incorporation of the functional groups in the preparation of the silica-ligand composite and the binding of targeted ions onto those ligands in a treatment operation become extremely slow and inefficient. Much prior art attempted to graft various ligand groups onto the surface of porous silica for ion-specific adsorption. However, because of the inefficiency, the loading and adsorption capacities of those ligands were consistently lower than 1 mmole per gram of silica^{8,9,10,11,12,13,14,15,16}.

The aforementioned new class of surface-modified low-density silica gel (CSMG), as described in the aforementioned U.S. Serial No. 09/601,888 and PCT/US99/02181, is produced by chemically modifying a freshly produced (i.e. gelled without prolonged aging) silica gel still in its wet state with molecular recognition ligand groups. This new class of

⁸ D. E. Leyden and G. H. Luttrell, Analytical Chemistry 47(9): pp 1612-1617 (1975)

⁹ D. E. Leyden and G. H. Luttrell, Analytical Chimica Acta, 84, pp 97-108 (1976).

¹⁰ M. C. Gennaro, E. Mentasti, and C. Sarzanini, pp 1013-1015 (1985)

¹¹ K. Ohshima, H. Watanabe, and K. Haraguchi, Analytical Sciences 2: pp 131-135 (1986)

¹² A. Tong, Y. Akama, and S. Tanaka, Analytica Chimica Acta 230: pp 179-181 (1990)

¹³ I. P. Alimarin, V. I. Fadeeva, et al., Talanta 34(1): pp 103-110 (1987)

¹⁴ T. I. Tikhomirova, V. I. Fadeeva, et al. Talanta 38(3): 267-274 (1991)

¹⁵ H. Ince, S. Akman, and U. Koklu, Fresenius Journal of Analytical Chemistry 342: 560-562 (1992)

¹⁶ E. M. Soliman, Analytical Letters 30(9): 1739-1751 (1997)

silica-ligand composite, CSMG, has a characteristic open pore structure, as well as an exceptional high loading of surface ligands, both resulting from controlling the interfacial energy and processing kinetics during its preparation.

5 Compared with existing art in the field, CSMG differs in the following four categories:

(1) Composition: much higher loading of ligands (7.5 mmole per gram of support),

10 (2) Morphology: open channels connecting micro- and nanopores,

(3) Adsorption efficiency: majority of the loaded ligands are accessible,

(4) Processing efficiency: significantly reduced processing time,

15 (5) Solvent systems of processing: environmentally benign solvents.

As described in the aforementioned applications, the surface density of fully dense monolayer coverage for CSMG was estimated to be 5×10^{18} molecules per square meter of surface area. The ligand loading percentage on the silica surface achieved is close to 100%, based on the loading of 7.5 mmole ligand per gram of silica, (for a specific surface area of 900 m²/g silica). It is readily apparent that the utilization of the surface ligands of the CSMG for binding metal ions is far more efficient, e.g., rapid and complete, than achieved with prior art silica particles. For instance, adsorption tests done by mixing adsorbent with waste solution for one hour indicated a utilization of the surface ligand group is greater than about 50% for the CSMG used in the present invention, as compared to at most, about 25% for the prior art silica particles. It is presumed that in CSMG, the dense ligand groups, randomly distributed on the convex particle surfaces, are spreading outward and are more accessible for binding metal ions from the solution.

35 The metal ion adsorption capacity of the CSMG (140 mg adsorbent in 200 ml solution, for 1 hour, pH 23) as previously reported in SN 60/074,026, was as follows:

	Capacity (mg/g)
Ag ⁺	707
Pb ²⁺	253
Hg ²⁺	737
Cu ²⁺	243

5 These data demonstrated that the metal ions adsorbed on
the CSMG surface (concentration approx. 5×10^{18} molecules per
square meter) are far more condensed than the population in
the waste stream (estimated as 10^{16} molecules per square meter
cross sectional area for part per thousand waste
10 concentration). If there are other species reactive to the
metal ions existing near the surface of the adsorbent, the
condensed state resulting from the strong surface adsorption
is likely to increase the reaction rate significantly.

15 The present invention takes advantage of the high
adsorbed metal ion concentration by intermixing, as described
below, reactive particles with adsorbent particles.

20 The composition as well as the microstructure according
to this invention contains at least three different phases:
adsorbent particles, reactant particles and interstitial
pores. The size of the reactant particles is at least several
times larger than the size of adsorbent particles so that the
interstitial pores are predominantly residing with the
adsorbent particles. (The smaller particles and their
interstitial pores fill the interstitial region of the larger
25 particles.) The total volume fraction of the larger particles
is controlled so that the larger particles are in domains
surrounded by smaller particles and their interstitial pores.
In the continuous phase composed of the smaller particles and
their interstitial pores, the relative volume fraction of the
30 pores to that of the smaller particles is larger than the
percolation threshold value so that the continuous phase
contains connected open pores. The material disclosed in this
invention with the described unique composition and
microstructure is hereafter referred to as the Nanopore
35 Reactive Adsorbent.

Figures 1-A and 1-B are illustrations of embodiments of this concept wherein reference numeral 10 identifies the reactant particles, reference numeral 12 identifies the adsorbent particles and reference numeral 14 identifies the interstitial pores. In Fig. 1-A the larger reactant particles 10 are embedded within the continuous phase substantially as isolated or discontinuous phases. In Fig. 1-B, the larger reactant particles 10 are in contact with each other, forming a second continuous phase, namely, a bi-continuous structure.

Because the size of silica particles and pores in a CSMG is in the range of several to about ten nanometers, it is possible to embed a large amount of micron-sized (or larger) solid reactant particles into the gel structure without blocking the flow and diffusion of the liquid stream that carries the waste species. As long as one continuous phase of such a composite is composed of the nanopore silica, the liquid can flow around these embedded particles through the open channels within the silica phase.

The presence of a reactant in the condensed solid state near the pore surfaces that are already adsorbed with a dense layer of the second reactive specie creates the opportunity for a rapid reaction between the two species. Enclosing the solid reactant particles with the nanopore silica immobilizes the solid reactant phase, thus, for example, facilitating use within a filtration column. The increased reaction rate as well as the prolonged residence time of the reactive waste species due to surface adsorption allows a high degree of reaction during a filtration treatment of a waste specie or other desirable or undesirable specie for recovery or discharge of the specie and/or discharge of the treated liquid.

For example, according to a specific embodiment of the present invention iron particles are embedded in a CSMG or precipitated silica or other metal oxide adsorbent to enhance the capacity of adsorbing silver ions from photographic waste. The CSMG adsorbent, due to the high loading of mercaptan

containing functional groups, can adsorb high amounts of silver ions and reduce its concentration in the waste to parts per billion with a single treatment. The embedded iron particles can react with the surface-adsorbed silver ions and reduce them to silver metal. Because of the increased reactivity by dense surface adsorption, the chemical reaction can occur during the filtration process, leaving the silver metal deposits within the CSMG column. The reduction of silver ion to metal form deposited within the column is beneficial to the treatment in at least three ways:

- The silver ions being reduced to metallic form, are ready for recovery.

- The metal silver particles are highly condensed and can be deposited in large quantities within the filtration column.

- The silver ions adsorbed on the CSMG surface are reduced to metal, releasing the surface active site for further adsorption and increasing the capacity of waste treatment.

The following examples illustrate this embodiment of the present invention.

Example 1: CSMG embedded with Iron particles

Silica sol is prepared from tetraethoxysilane (TEOS), H₂O, ethanol and HCl, in the total molar ratio 1:2:4:0.0007. The mixture of 50 ml of silica sol and an amount (depending on the desired % of ligand loading) of 3-mercaptopropyltrimethoxysilane is added into a reaction vessel equipped with agitator, heating mantel, thermometer and nitrogen purge system. Additional amounts of water or ethanol are used to adjust the water/ethanol ratio in the solvent mixture so that their properties are suitable for the amount of ligand desired. After the reaction mixture is heated to 50-60°C for 1-2 hours, a desired amount of Fe powder is added with vigorous stirring. Then, a NH₄OH solution is added to the mixture to induce gelation.

After cooling, the Fe powder-loaded CSMG is aged over night and successively washed thoroughly with ethanol and water.

Example 2: Precipitated Silica embedded with Iron particles

A diluted sodium silicate solution is strongly stirred. To this solution, a desired amount of Fe powder (depending on the desired concentration of Fe in the gel) is added. Then an
5 acidic solution is added to the mixture to induce gelation. The kinetics of the gelation reaction must be controlled so that the porosity and the amount of surface active silanol groups are optimized for silver ion adsorption. The Fe powder-loaded silica is aged over night and then dried.

Characterization and Analysis

Adsorption efficiency and capacity were determined for bare CSMG and precipitated silica respectively by flowing 2000 ppm Ag⁺ standard through a column of the adsorbent. Effluent
15 samples are collected periodically for the analysis of residual silver ion concentration. The treatment capacity of CSMG is about three times of that of precipitated silica because of the dense mercaptan groups already incorporated on the surface of CSMG silica. However, the precipitated silica embedded with iron particles prepared according to Example 2
20 with silica to iron weight ratio as 3 to 1 exhibits a capacity exceeding that of bare CSMG.

Enclosing iron particles increased the treatment capacity of precipitated silica three fold. The improvement may be even greater by increasing the weight ratio of iron to silica.
25 The comparison of the respective adsorption capacity is demonstrated in Fig. 2.

Although described primarily with respect to silica gels the composite nanopore reactive adsorbent of the present invention may be formed starting from other metal oxides, such
30 as, for example, zirconia, titania, alumina, iron oxide, lanthanum oxide, and the like.

The composite nanopore reactive adsorbent may be used in bulk form, as described above, or adsorbent particles may be shaped into various forms, so long as the basic properties are
35 not modified. The adsorbent may also be distributed in and among porous or microporous filter media inert to the liquid to be treated. For example, a paper or plastic filter or

membrane material may be incorporated with the composite adsorbent to further facilitate removal of unwanted contaminants or other valuable specie in a liquid media. A multilayer filter media may include, for example, a layer of the composite nanopore reactive adsorbent in one layer and bare CSMG or other metal adsorbent in a second or adjacent layer.

The present invention thus provides a new class of material, referred to herein as Nanopore Reactive Adsorbent. This class of material is composed of adsorbent particles of nanometer size at a low density with interconnecting nanopore structure. The nature of low-density and nanopore size, assures a high specific surface area which will facilitate high-efficiency adsorption and surface modification. Reactant or catalyst, as described herein, with a particle size much larger than the average pore size, are embedded within and among the nanopore adsorbent to promote reaction along with the adsorption. Furthermore, the adsorbent surface can be chemically modified to enhance the adsorption capacity, selectivity or reactivity of the adsorbed species. Compared with traditional waste treatment methods by adsorption, reaction, or heterogeneous catalysis, the new Nanopore Reactive Adsorbent offers the following performance advantages:

(1) Direct conversion of waste species into useful or a less harmful product: In the example given, silver ions were reduced by iron particles into silver metal. Bacteria or enzyme may be used in a similar fashion to convert other waste species, proteins, etc.

(2) The reaction increases the treatment capacity and efficiency of the adsorbent: The reaction of adsorbed specie into a product can refresh the surface sites for additional adsorption. The capacity is higher because of the reactive conversion.

(3) The adsorption enhances the reaction rates of the reactants: The adsorption of a reactive specie from the waste stream (like the retention of a specie in a chromatography

column) prolongs its residence time in the column. During the residence time the embedded reactant or catalyst can effectively convert the adsorbed specie into product.

(4) Significantly increased speed of treatment: The adsorption holds back the progression of the material front of the waste specie, thus allowing the waste stream to be fed with a much higher flow rate.

(5) Close-end regeneration of the adsorbent by reactive adsorption: When a normal adsorbent column reaches its adsorption capacity, it can be regenerated by backwash with an appropriate treating liquid, as well known in the art. However, the backwash effluent must be treated separately in order to remove the waste species. For example, the effluent from regenerating a cation-exchange resin must be precipitated by sodium hydroxide solution. In the case of a reactive adsorbent, the effluent can be fed back into the column for engaging additional reaction. The example below illustrates this unique feature of the reactive adsorbent.

For example, during the use of an iron-embedded silica column to treat a heavy metal waste solution, a breakthrough point will be reached when the ion concentration in the exiting effluent approaches the discharge limit allowed for that particular ion. Normally at this point, a large amount of iron particles embedded in the silica are still not yet consumed. However, the reaction rate of the heavy metal ions with iron will have decreased to a point such that the traveling time through the column is no longer enough for a thorough reaction. The reduced reaction rate is partially due to the build-up of ferrous oxide deposits on the surface of the iron particles. A major reduction in treatment efficiency is also due to the exhaustion of surface adsorption sites on the silica surfaces.

The present invention therefore, provides a method for regenerating the column of spent or partially spent Nanopore Reactive Adsorbent by backwashing with an acidic solution back and forth.

Thus, the first batch of backwash not only provides clean up the oxides of the iron particles, but also replaces the adsorbed heavy metal ions on the silica surface by hydronium ions. Furthermore, the effluent of backwashing can be flowed back through the column to remove the heavy metal ions by reacting with iron particles. In a normal ion-exchange system there will be no net gain by flowing a backwash solution through the column again. However, because of the reactive nature of the Nanopore Reactive Adsorbent, the heavy metal ions in the first batch will be retained by adsorption to the regenerated silica surface and therefore will have time to be reduced by the regenerated iron particles to metallic silver. After repetitive backwash, the silica surface and the iron particles are fresh again for additional reactive adsorption. In addition, the heavy metal ions previously adsorbed on the silica surface are converted by the reactant to their metallic form.

This aspect of the present invention is illustrated by the following example.

Example 3: Regeneration of iron-embedded silica adsorbent

The iron-embedded silica made from Example 2 was packed into a column for treating simulated waste solution with 1620 ppm initial silver concentration. After passing 125 bed volume of solution, the column was regenerated with 2 M acetic acid. After regeneration, the flow was continued until reaching 187 bed volume. The results are shown in Fig. 3.

As noted above, one of the specific applications of the present invention is the recovery of silver (from silver ions) in spent photographic waste (e.g., photodeveloping liquids), using, e.g., iron, as the reactant particles. Conventionally, this is accomplished by flowing the silver containing liquid through steel wool filters (functioning as batch or plug-flow reactor). However, in this case, there is no adsorption of the silver ions by the batch or plug flow reactor. Therefore, it is necessary to very slowly flow the waste liquid through the steel wool. Accordingly, the present invention contemplates connecting the Nanopore Reactive Adsorbent, in

series, with the steel wool filter, thereby combining the capacity of the steel wool with the efficiency of the Nanopore Reactive Adsorbent. Accordingly, the treatment speed and overall flow rate can be increased by several to ten-fold greater than the flow through only the batch or plug-flow reactor.

While the above description is based primarily on the use of metal, e.g., iron, as reactant particles, those skilled in the art will recognize that the selection of the reactant particles will depend on the specie to be removed and/or recovered from the liquid supply. Thus, in the case of, for example, removing biological contaminants, such as microorganisms, e.g., bacteria, spores, viral particles and the like, the catalyst and the reactant particles may be an enzyme or other reactive substance for the particular biological contaminant.

The present invention may, for example, be used to remove mercury from hydrocarbon feedstocks, as in, for example, U.S. 5,107,060, using as reactant particles a substance selected from the group consisting of copper, gold, silver, iron, bismuth and tin, as metals, oxides and sulfides, or using solid sulfur particles, as disclosed in U.S. Patent no. 5,401,393. Other reactive particles for removing mercury are mentioned in the backgrounds of U.S. 5,107,060 and U.S. 5,401,393, the disclosures of which is incorporated herein by reference thereto.

The reactive adsorbents of this invention may be used, for example, with organic reactant particles, such as disclose in, for example, U.S. Patent No. 6,007,724, which discloses a process for treating a liquid feed stream containing an iodine-containing compound by contacting the liquid stream with an adsorbent comprising a solid carrier having deposited thereon a metal phthalocyanine compound where the metal is selected from the group consisting of silver, mercury, copper, lead, thallium, palladium, and mixtures thereof, at adsorption conditions effective to adsorb the iodine-containing compound on the adsorbent to yield a treated liquid stream. In

accordance with the present invention, the adsorbent comprises porous open-cell structure as described herein. The disclosure of U.S. 6,007,724 is incorporated herein in its entirety, by reference thereto.

- 5 U.S. Patent 5,990,373, titled "Nanometer sized metal oxide particles for ambient temperature adsorption of toxic chemicals" discloses removal of toxic target chemical compounds, such as, for example, HCN, $P(O)(OCH_2CH_3)(CN)(N(CH_3)_2)$, $ClCN$, $(CF_3)_2C=CF_2$, $Zn(CH_2CH_3)_2$,
10 $Hg(CH_3)_2$, $Fe(CO)_5$, $(P)(O)(CH_3)(F)[OCH(CH_3)_2]$, $S(CH_2CH_2Cl)_2$, $C_6H_5C(O)CH_2Cl$, $C(O)Cl_2$, C_6Cl_5OH , $C_6H_5(OH)(NO_2)_3$, $C_6H_5(Br)(CN)$, $C_6H_5CH_2CN$ and $(CF_3)C=CF_2$, using as adsorbent particles, MgO and CaO , preferably at a temperature in the range of -70 to $90^\circ C$ and at atmospheric pressure. The reactive adsorbent of the
15 present invention may also be used for the removal of the above mentioned toxic chemicals using MgO or CaO as the reactant particles, in accordance with the conditions as described in U.S. 5,990,373, the disclosure of which is incorporated herein in its entirety by reference thereto.
- 20 United States Patent 6,057,488, titled "Nanoparticles for the destructive sorption of biological and chemical contaminants" describes a method for destroying a target component, such as hydrocarbons, halogenated hydrocarbons, diethyl-4-nitrophenyl phosphate (paraoxon), 2-chloroethyl
25 ethyl sulfide (2-CEES), dimethylmethylphosphonate (DMMP), bacteria such as *Bacillus Cereus*, *Bacillus Globigii*, *Chlamydia* and/or *Rickettsiae*, fungi and viruses, by contacting the target component with a metal oxide adsorbent, such as MgO , wherein the adsorbent contains either reactive atoms selected
30 from the group consisting of halogens and alkali metals stabilized on the surfaces of the adsorbent or ozone and wherein the contacting is conducted at a temperature of -40 to $600^\circ C$ for a time period of at least about 4 seconds. The reactive adsorbent of this invention can be adapted to the
35 process disclosed in U.S. 6,057,488, the disclosure of which

is incorporated herein, in its entirety, by reference thereto, by utilizing the stabilized halogens or alkali metals as the reactant particles.

5 The reactant particles may also comprise, for example, polynuclear metal oxyhydroxides, as disclosed in U.S. Patent No. 6,103,126, for the selective elimination of inorganic phosphate from liquids, in particular from body fluids containing protein such as whole blood, plasma, liquid contents of the intestine as well as from dialysis fluid. The
10 disclosure of U.S. 6,103,126 is incorporated herein in its entirety by reference thereto.

WHAT IS CLAIMED IS:

1 Claim 1. A composite nanopore reactive adsorbent
2 comprising
3 a continuous phase comprised of adsorbent particles and
4 interstitial pores therebetween, and
5 a phase comprised of reactant particles contained in
6 isolated domains surrounded by the adsorbent particles and
7 their interstitial pores,
8 thereby forming an intimate admixture of adsorbent
9 particles, reactant particles and interstitial pores,
10 wherein the size of the reactant particles is at least
11 several times larger than the size of adsorbent particles such
12 that the interstitial pores predominantly reside with the
13 adsorbent particles,

14 wherein the relative volume fraction of the interstitial
15 pores in the continuous phase to that of the adsorbent
16 particles is larger than the percolation threshold value so
17 that the continuous phase contains connected open pores.

1 Claim 2. A nanopore reactive adsorbent, as set forth in
2 claim 1, wherein the adsorbent particles are formed from
3 precipitated silica.

1 Claim 3. A nanopore reactive adsorbent, as set forth in
2 claim 1, wherein the adsorbent particles comprise chemically
3 surface modified amorphous silica gel comprising

4 (i) a pore size distribution of pores having pore
5 diameters of about 10 nanometers; and

6 (ii) ligand loading of about 7.5 mmole ligand per gram
7 silica gel.

8 Claim 4. A nanopore reactive adsorbent according to any
9 one of claims 1 to 3, wherein the phase comprised of reactant
10 particles is a discontinuous phase.

1 Claim 5. A nanopore reactive adsorbent according to any
2 one of claims 1 to 3, wherein the phase comprised of reactant
3 particles is a continuous phase.

1 Claim 6. A nanopore reactive adsorbent according to any
2 one of claims 1 to 5, wherein the reactive particles are
3 comprised of metal effective as an in-situ reducing reagent.

1 Claim 7. A nanopore reactive adsorbent as set forth in
2 claim 6, wherein the metal is at least one metal selected from
3 the group consisting of magnesium, aluminum, iron, and zinc.

1 Claim 8. A nanopore reactive adsorbent as set forth in
2 any one of claims 1 to 5, wherein the reactive particles are
3 comprised of a solid redox reagent effective to react with an
4 adsorbed species.

1 Claim 9. A nanopore reactive adsorbent as set forth in
2 any one of claims 1 to 5, wherein the reactive particles are
3 comprised of a microorganism or enzyme which is effective to
4 react with an adsorbed species.

1 Claim 10. A nanopore reactive adsorbent as set forth in
2 claim 9, wherein the microorganism comprises bacteria.

1 Claim 11. A method for producing the composite nanopore
2 reactive adsorbent as set forth in claim 1 comprising:

3 (a) reacting an inorganic metal oxide nanoporous gel
4 precursor characterized by a plurality of open channels within
5 the gel structure and hydroxyl reactive groups on the surface
6 thereof, with a coupling reagent reactive with said hydroxyl
7 reactive groups, in an aqueous alcoholic medium under an inert
8 atmosphere and at an elevated temperature within the range of
9 from about 40 EC to about 80 EC to cause the coupling reactant
10 to condense and react with said hydroxyl reactive groups to
11 form a grafted metal oxide sol;

12 (b) mixing and stirring the grafted silica sol with
13 reactant particles; and

14 (c) gelling the stirred mixture from step (b).

1 Claim 12. The method according to claim 11 wherein the
2 gel precursor comprises a silica gel precursor.

1 Claim 13. The method according to claim 11 wherein the
2 gel precursor comprises an oxide of a metal selected from the
3 group consisting of silicon, zirconium, aluminum, titanium,
4 iron and lanthanum.

1 Claim 14. A method for separating a target specie from a
2 liquid containing the target specie which comprises contacting
3 the liquid with the nanopore reactive adsorbent as set forth
4 in any one of claims 1 to 10.

1 Claim 15. The method according to claim 14, wherein the
2 target specie comprises silver ions and the reactant particles
3 of the reactive adsorbent comprises iron particles, whereby
4 the adsorbed silver ions are reduced by the iron particles to
5 metallic silver.

1 Claim 16. The method according to claim 15, wherein the
2 nanopore reactive adsorbent is present in or as a filter
3 medium.

1 Claim 17. The method according to claim 15, which
2 further comprises recovering the metallic silver from the
3 adsorbent.

1 Claim 18. The method according to claim 14, which
2 further comprises, prior to contacting the liquid with the
3 nanopore reactive adsorbent, flowing the liquid through a
4 batch or plug-flow reactor effective for removing said target
5 specie from the liquid, and thereafter flowing the treated
6 liquid, through the nanopore reactive adsorbent, thereby
7 allowing a substantially higher flow rate to achieve the
8 desired degree of removal of said specie as compared to the
9 flow rate through only the batch or plug flow reactor.

1 Claim 19. The method according to claim 15, which
2 further comprises, prior to contacting the silver containing
3 liquid with the nanopore reactive adsorbent, flowing the
4 silver containing liquid through a batch or plug-flow reactor
5 effective for removing silver from the liquid, and thereafter
6 flowing the treated liquid, through the nanopore reactive
7 adsorbent, thereby allowing a substantially higher flow rate
8 to achieve the desired degree of removal of said specie as
9 compared to the flow rate through only the batch or plug flow
10 reactor.

1 Claim 20. A closed end regeneration method which
2 comprises adsorbing a specie from a starting liquid containing
3 the specie by contacting the liquid with a nanopore reactive
4 adsorbent comprising connected interstitial pores having
5 adsorption sites on the surfaces thereof, and containing among
6 the interstitial pores thereof reactant particles which are
7 reactive with said specie, thereby removing at least some of

8 said specie from said liquid and forming spent adsorbent,
9 flowing a treating liquid through the spent adsorbent, said
10 treating liquid being capable of regenerating the reactant
11 particles and at the adsorption sites of the interstitial
12 pores, to thereby regenerate at least some of said reactant
13 and adsorbent particles and forming an effluent treating
14 liquid, and flowing the effluent treating liquid at least two
15 times through the nanopore reactive adsorbent to regenerate
16 said reactant and adsorbent particles, while converting the
17 specie removed from the adsorption by *in situ* reaction.

1/2

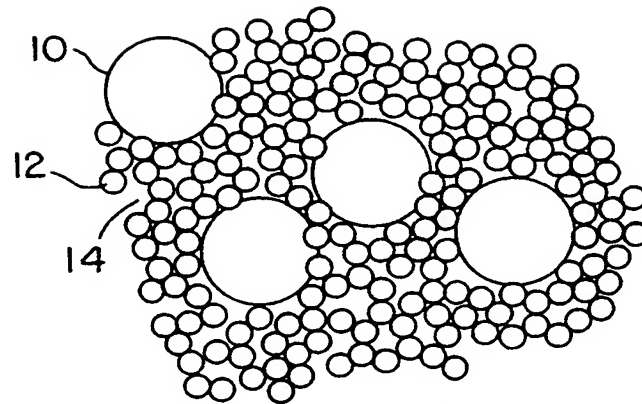


FIG. 1A

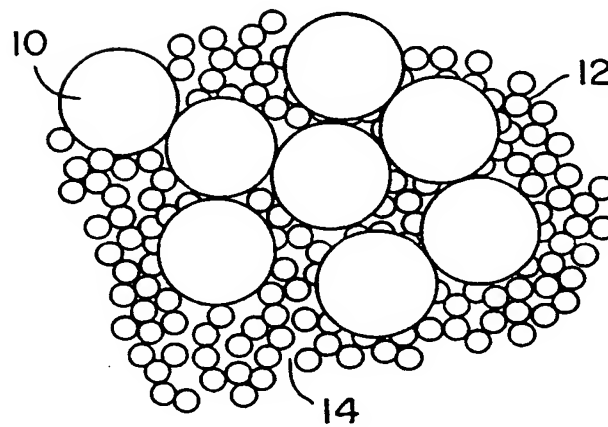


FIG. 1B

2 / 2

Comparison of Ag + Adsorption

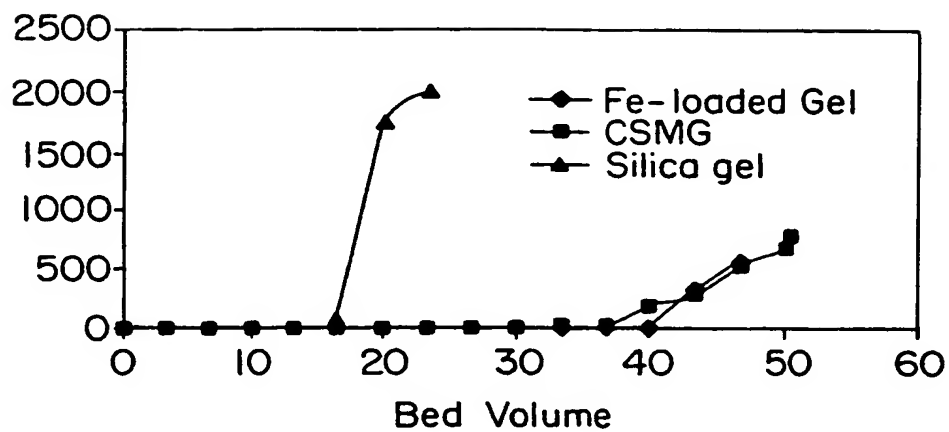


FIG. 2

Adsorption with Regeneration

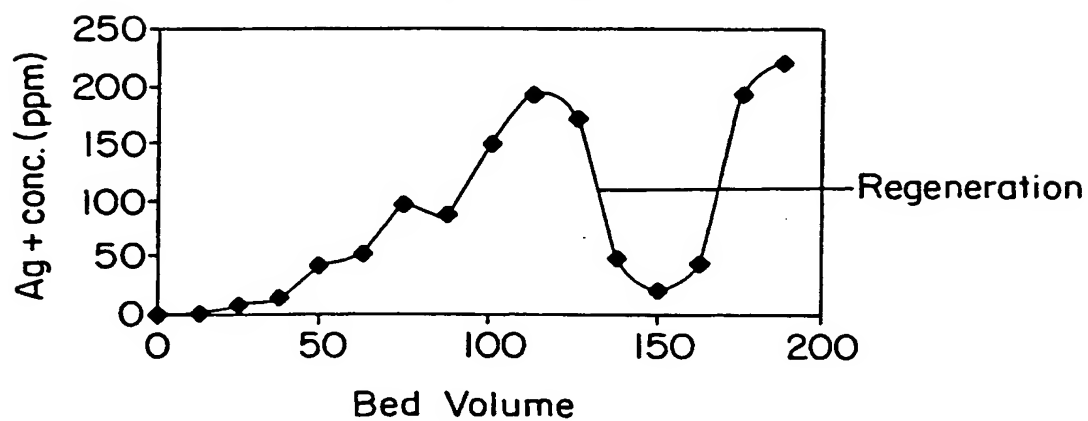


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/24472

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 15/00; A62D 3/00

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, A	US 6,057,488 A (KOPER et al) 02 May 2000 (02.05.00), see entire document.	1, 4-7, 11
Y, A	US 6,007,724 A (KULPRATHIPANJA et al) 28 December 1999 (28.12.99), see entire document.	1-7, 11-13, 20
Y, A	US 5,990,373 A (KLABUNDE) 23 November 1999 (23.11.99), see entire document.	1, 4-7, 11-13
Y, A	US 6,103,126 A (BOOS et al) 15 August 2000 (15.08.00), see entire document.	1-7, 11-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

30 OCTOBER 2000

Date of mailing of the international search report

18 DEC 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SUN UK KIM

Jean Proctor
Paralegal Specialist

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/24472

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 8-10, 14-19
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/24472

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

210/483, 488, 490, 502.1, 510.1, 638, 660, 670, 673, 679, 683, 690, 691; 423/70, 100, 101, 104, 112, 139, 140, 324, 325, 326, 327.1, 335, 338; 502/400, 405, 407, 414; 588/200, 205, 223, 231, 242

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

210/483, 488, 490, 502.1, 510.1, 638, 660, 670, 673, 679, 683, 690, 691; 423/70, 100, 101, 104, 112, 139, 140, 324, 325, 326, 327.1, 335, 338; 502/400, 405, 407, 414; 588/200, 205, 223, 231, 242

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-7, drawn to a composite nanopore reactive adsorbent comprising a continuous phase comprised of adsorbent particles and interstitial pores therebetween and a phase comprised of reactant particles contained in isolated domains surrounded by the adsorbent particles and their interstitial pores and claims 11-13, drawn to a method for producing the composite nanopore reactive adsorbent comprising reacting an inorganic metal oxide nanoporous gel precursor with a coupling reagent reactive with hydroxyl reactive groups in the gel precursors.

Group II, claim 20, drawn to a closed end regeneration method comprising the step of flowing a treating liquid through the spent adsorbent wherein the treating liquid is capable of regenerating the reactant particles and at the adsorption sites of the interstitial pores.

The inventions listed as Groups I-II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: All of the groupings are directed to a method or apparatus for a composite nanopore reactive adsorbent, but each group has a different special technical feature not shared by the remaining groups. Group I is directed to a composite nanopore reactive adsorbent which has a special technical feature of a continuous phase comprised of adsorbent particles and interstitial pores therebetween and a phase comprised of reactant particles contained in isolated domains surrounded by the adsorbent particles and their interstitial pores not shared by any of the remaining groups. Group II is directed to a closed end regeneration method which has a special technical feature of flowing a starting liquid through a nanopore reactive adsorbent and then flowing treating liquid through a spent adsorbent not shared by any of the remaining groups.